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ORGANIC ELECTROCHEMISTRY IN ALUMINUM CHLORIDE MELTS.(U)
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Organic electrochemistry and chemical studies have been carried out in molten sodium tetrachloroaluminate at 175°C and in an ethylpyridinium bromide-aluminum chloride melt, with benzene as a cosolvent at room temperature. The reductive defunctionalization of a number of adamantanes was studied in the sodium tetrachloroaluminate system at 175°C. In the room temperature melt, with benzene, the oxidation of hexamethylbenzene was studied and was found to yield pentamethylbenzene and diphenylmethane. (cont)		

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The pentamethylbenzene could be further oxidized to tetramethylbenzene and diphenylmethane. A mechanism is proposed. Several iron diimine complexes were also studied in this melt. Voltammetric half-wave potential studies of iron(II)-phenanthroline complexes and N.M.R. studies on the melt-benzene system are interpreted as indicating that the acidity of the system is decreased as benzene is added, indicating the formation of a benzene:AlCl₃ complex. The electrochemical behavior of several simple metal cations was studied in the room temperature melt, as was the behavior of the carbonyls of chromium, tungsten, molybdenum and iron.

ORGANIC ELECTROCHEMISTRY IN ALUMINUM CHLORIDE MELTS

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ORGANIC ELECTROCHEMISTRY IN ALUMINUM CHLORIDE MELTS

The work reported here has involved efforts to study aspects of organic electrochemistry in strong Lewis acid molten salt systems. Work has been performed in sodium tetrachloroaluminate melts at 175°C ($\text{AlCl}_3\text{:NaCl}$ mole ratio ~1:1) and an ethylpyridinium-aluminum chloride melt ($\text{AlCl}_3\text{:EtPyBr}$ mole ratio ~2:1) which is liquid at room temperature.

Initial activity involved an investigation of the behavior and electrochemical activity of a number of adamantanes in the NaCl:AlCl_3 system at 175°C. This work has been published,¹ and is summarized below.

The reactivity of a number of substituted adamantanes in molten NaAlCl_4 at 175° was assessed. Those substituents with Lewis base character reacted with the melt to give adamantane and chloroadamantane. Neutral and Lewis acid substituents were recovered unchanged. Cyclic voltammetry revealed adamantane and 1-methyladamantane to be electroactive at a tungsten electrode well within the background limits of molten NaAlCl_4 . The result of adding 1-Ad-X to the melt is summarized in Table I.

Table I

Adamantyl Compounds Defunctionalized by 50:50

Mol % $\text{AlCl}_3\text{-NaCl}$ Melt

Registry No.	X	1-Ad-X, mmol	% conversion	
			Ad-H	1-Ad-Cl ^a
768-92-3	F	0.36	25	0.2
935-56-8	Cl	0.80	28	0.2
768-90-1	Br	1.23	28	0.2
6221-74-5	OMe	0.63	38	9.5
768-95-6	OH	0.84	41	8.0
768-94-5	NH ₂ ^b	1.12	16	1.3
	NH ₂ ^c	1.18	13	1.7
828-51-3	Co ₂ H ^d	0.57	23	0.4
711-01-3	Co ₂ Me ^d	0.97	21	0.4

^aTrace amounts of 2-Ad-Cl detected. ^b0.30 mmol of 1-Ad-NH₂ recovered. ^cReaction time doubled; 0.29 mmol of 1-Ad-NH₂ recovered. ^dCarbon monoxide evolved.

Table II
Voltammetry

Substrate	$E_p/2^a$	$E_p/2^b$
phenyldecane	1.93	--
tetraline	1.63	1.83
durene	1.29	1.74
hexamethylbenzene	1.16	1.56
adamantane	1.65	2.36
ferrocene	0.12	0.55

^aPt anode, 0.2 V/sec, 10^{-1} M Ag^+/Ag in acetonitrile @ 25°C.

^bVitreous carbon anode, 0.2 V/sec, Al wire in sat $NaCl-AlCl_3$ melt @ 175

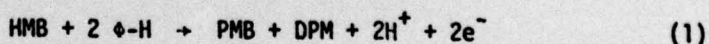
A consideration of the E_p^a values in Table II is of interest. With the exception of durene, which partially isomerizes to 1,2,3,5-tetramethylbenzene, the others were stable to the melt at 175°C. In comparing $E_p/2$ values for the same substrates in different media at different reference electrodes, it is necessary to have at hand a compound which manifests simple redox behavior in a variety of diverse solvent/reference systems. Ferrocene undergoes a reversible one-electron transfer in many aprotic solvents as well as in $AlCl_3$ - $NaCl$ melts, and the $E_{1/2}$ has been shown to be insensitive to solvent variation. Accordingly, it may be seen that the apparent shift of the alkyl-aromatics to more positive potentials is primarily an artifact of the difference in reference electrodes. The $E_p/2$ for adamantane is, on the other hand, distinctly shifted to more negative potentials. This shift is presently unexplained.

The high temperature required for the use of the $NaCl:AlCl_3$ system (175°C) mitigates against its use for many organic compounds. Therefore, effort was made to determine if a lower temperature Lewis acid system could be found. These efforts resulted in establishing a new, room temperature molten salt system. The low temperature fused salt was prepared by combining aluminum

chloride with ethylpyridinium bromide, the admixture spontaneously melting to a golden liquid. After purification by constant current electrolysis between two aluminum rods a clear, colorless fluid resulted. The operating range of the melt extended from 20 to 100°C. At 25°, the temperature at which most of the experiments were conducted, the viscosity was found to be 25 cp and the conductivity, $3 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$.

A variety of electrode materials were surveyed via cyclic voltammetry to ascertain which afforded the widest electrochemical window. Tungsten and vitreous carbon proved to be the most suitable, both spanning a two-volt range prior to the onset of background processes (0 to +2V vs. an Al reference). Gold and platinum reacted with the melt, and mercury was limited by a narrow (600 mV) potential range.

Organic electrosynthesis was conducted in a 50-50 by volume molten salt-benzene solution. This mixed solvent afforded improved conductivity ($11 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$, 25°) and solubility of organic substrates. When one equivalent of hexamethylbenzene (HMB) was potentiostatically oxidized at either a glassy carbon or tungsten working electrode, one equivalent each of pentamethylbenzene (PMB) and diphenylmethane (DPM) resulted (eq. 1).



The material balance and current yields for this two-electron oxidation approach 100%.

This work is currently in press in J. Am. Chem. Soc.² An abstract of that work follows.

"The electrochemical oxidation of hexamethylbenzene was studied in a room temperature molten salt system, namely a 67:33 mole percent aluminum chloride: ethylpyridinium bromide melt and in a 50-50 by volume solution of the melt with benzene.

Oxidation of hexamethylbenzene in the melt itself yielded a mixture of

alkylated polyphenyl compounds and small amounts of alkylated diphenylmethanes. Preparative oxidation in the melt plus benzene yielded nearly one equivalent each of pentamethylbenzene and diphenylmethane. The pentamethylbenzene could be oxidized further to yield tetramethylbenzene and more diphenylmethane. Coulometry, cyclic voltammetry and ring-disc electrode studies were carried out to elucidate a mechanism for the reaction. It was shown that hexamethylbenzene²⁺ was initially formed; it then reacts by a second order process which eventually leads to the pentamethylbenzyl cation. It was shown that under the reaction conditions, this cation leads to the observed products."

In conjunction with Professor Helena Li Chum (University of Sao Paulo, Brazil) we have also studied the electrochemistry of two iron diimine complexes in the room temperature molten salt at a glassy carbon working electrode. It was found that the redox behavior of the complexes in our high Lewis acid medium paralleled that previously measured in 11 M sulfuric acid. Thus, one can conceivably substitute the molten salt for protic acids when hydronium ions and the attendant water molecules are undesirable for a given reaction.

This work, and results of preliminary experiments on the hexamethylbenzene have been published.³

As mentioned above, we have found that the ethylpyridinium-aluminum chloride melt system forms a useful solvent system mixed with benzene, and possible other aromatic materials, as a cosolvent. Experiments had indicated that the half-wave potentials for the normal pulse voltammograms of previously studied iron complexes such as $\text{Fe}(\text{Phen})_3^{2+}$ is displaced in the anodic direction as benzene is added to the molten salt mixture. The complex is reversibly oxidized, as judged from the log plots of the normal pulse voltammograms. This effect is the same as that found for these complexes in H_2SO_4 where the half-wave potential shifts in the anodic direction as the acidity decreases. Under identical conditions, ferrocene in the melt or melt and benzene mixture

shows no change in its half-wave potential; this indicates that junction potential problems are at least minimal.

To investigate this change in acidity further, NMR spectra were obtained. ^{27}Al spectra, obtained for us by Varian, indicated that the dominant species in the pure 2:1 $\text{AlCl}_3:\text{EtPyBr}$ melt could not be AlCl_4^- but might be either Al_2Cl_6 or Al_2Cl_7^- . By analogy to work carried out elsewhere on pyridinium chloride-aluminum chloride melts, it is most logical to assume that the pure melt is essentially $\text{EtPy}^+ \text{Al}_2\text{Cl}_6\text{Br}^-$. Examination of the proton spectra indicated that the effect of benzene was to diminish the acidity of the system, probably by the formation of a benzene: AlCl_3 π -complex. Using tetramethylsilane as an internal reference, large, upfield chemical shifts for the methyl and methylene protons on the ethylpyridinium moiety are found; the benzene protons also shift upfield, though to a smaller extent. By considering several equilibria, efforts were made to obtain equilibrium constants for the proposed chemical reactions. However, the data is not sufficiently accurate to permit this, but certainly does indicate from a qualitative view point the nature of the melt-benzene interaction.

The electrochemistry of several inorganic cations - Ag^+ , Cu^+ and Fe^{++} - was briefly investigated.

A number of metal carbonyls were investigated; $\text{Cr}(\text{CO})_6$ appears to undergo a reversible, one-electron oxidation. This behavior is similar to that observed by others in acetonitrile.^{4,5} $\text{W}(\text{CO})_6$ and $\text{M}(\text{CO})_6$ were oxidized, but the products appeared unstable. $\text{Fe}(\text{CO})_5$ appears intermediate between the Cr and W-Mo carbonyls, in that the oxidation product is stable but undergoes some decomposition on the time scale of the electrochemical experiments.

Efforts were also made to prepare other, similar room temperature melts. An all-chloride melt of n-butylpyridinium chloride-aluminum chloride was successfully prepared.

A number of physical properties of these room temperature systems - viscosities, densities, conductivities - in the pure state and with benzene were measured.

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